PB86-185543

Stability of Turbidity in Raw Water and Its Relationship to Chlorine Demand

(U.S.) Environmental Protection Agency
Cincinnati, OH

Feb 86

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/J-86/019	2.
3. REC	PB86-185543
4. TITLE AND SUBTITLE THE STABILITY OF TURBIDITY OF RAW WATER AND ITS RELATIONSHIP TO CHLORINE DEMAND (Journal Version)	5. REPORT DATE 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E.L. Katz	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Water Engineering Research Laboratory U.S. Environmental Protection Agency Cincinnati, OH 45268	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. Inhouse
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory-Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Journal Article
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer, E.L. Katz
J. American Water Works Association, 78(2):72-75, Feb. 1986

16. ABSTRACT

In this study, 160 raw water samples collected throughout the United States were examined for chlorine demand, turbidity, and other chemical parameters to determine whether these parameters were interrelated. Eighty-nine of these samples were examined over a 1-week period to determine the stability of the turbidity values over 1, 3, and 7 days. Changes in turbidity were on the order of 77% of samples in the range of 0.05 to 1 ntu; 90 percnet of samples in the 1 to 5 ntu range; and 96% of those >5.0 ntu. In some cases, more than a 200-% change in turbidity is reflected. In 63% of the samples, changes of 10 to 50% were seen. Because of this strong indication of inherent instability of turbid raw water samples, measurements of samples should be done immediately on site to ensure accuracy of turbidity readings.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 6
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA/600/J-86/019
JOURNAL ARTICLE

The Stability of Turbidity in Raw Water and Its Relationship to Chlorine Demand

Edward L. Katz

In this study, 160 raw water samples collected throughout the United States were examined for chlorine demand, turbidity, and other chemical parameters to determine whether these parameters were interrelated. After raw water samples were examined, they were filtered through 0.45-μm membrane filters, and the filtrate and residue were then analyzed. Other parameters such as total organic carbon, total Kjeldahl nitrogen, volatiles, suspended solids, particle size, and inorganics were also examined. Eighty-nine of these samples were also examined over a one-week period to determine the stability of the turbidity values over one, three, and seven days. Changes in turbidity were on the order of 77 percent of samples in the range of 0.05–1 ntu, 90 percent of samples in the 1–5 ntu range, and 96 percent of those >5.0 ntu. In some cases, more than a 200-percent change in turbidity is reflected. In 63 percent of the samples, changes of 10–50 percent were seen. Because of this strong indication of inherent instability of turbid raw water samples, measurements of samples should be done immediately on site to ensure accuracy of turbidity readings.

For many years turbidity has been an important measure of drinking water quality. Although turbidity is used as a measure of the amount of particulate matter present in water, it is, at best, only an indirect measurement because it merely expresses "the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample."[1] The amount of scattering and absorption can vary tremendously, depending on the characteristics of the particles suspended in the water. Nevertheless, turbidity, measured as a limit of 1 ntu, has been included as a maximum contaminant level (MCL) in the National Interim Primary Drinking Water Regulations. This level can readily be attained by complete treatment. Consistently attaining this level is often difficult, however, if the only treatment is disinfection.[2] Current regulations also state that the turbidity MCL of 1 ntu can be exceeded to a limit of 5 ntu if three conditions are met: (1) higher turbidity does not interfere with disinfection, (2) the utility can show that the presence of turbidity does not interfere with maintenance of a disinfectant residual in the distribution system, and (3) turbidity does not interfere with microbiological determinations.

Little information is available on the disinfectant demand caused by particles suspended in water. In addition, although there are recommendations regarding storage time and conditions under which samples should be examined for turbidity,[3-5] the recommendations vary, and there is little experimental evidence to support them. Currently three basic storage methods are employed: storage of samples in the dark for up to 24 h,[6] storage at 4°C for up to 7 days,[7] and examination within 1 h.[8]

To gather background information on the relationship of turbidity to chlorine demand and the effects of storage time on turbidity of water samples, 160 raw water samples were examined. In addition to the relationship of turbidity to chlorine demand, the effects of total organic carbon (TOC), volatile organic carbon (VOC), total Kjeldahl nitrogen (TKN), inorganics (Fe and NH_4^+), and particle size on chlorine demand were examined. The raw water samples were filtered, and chlorine demand tests were performed on raw water, filtrate, and residue.

Experimental procedures

Sample collection. Raw waters were collected from a variety of drinking water sources throughout the United States.

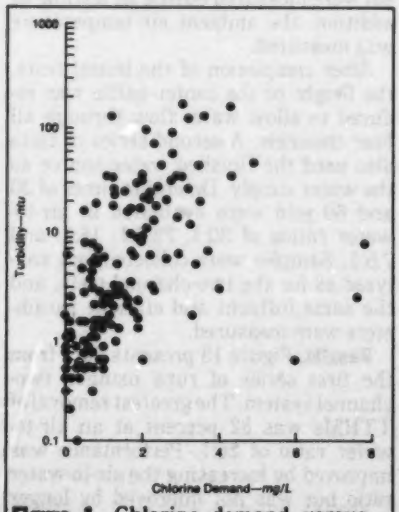

Figure 1. Chlorine demand versus turbidity

78(2):72-75, Feb. 1986

Initially, 12 samples were collected at the Cincinnati Water Works (Ohio River source) and at other local utilities. An additional 12 samples were collected within a 250-mi (402-km) radius of Cincinnati. The remaining 136 samples were collected as part of a study of organic chemicals in water supply source waters.[9] The latter samples were in transit under refrigeration for up to 3 days before examination. No preservatives had been added to any of the samples collected.

The samples included both surface water and groundwater. Most of the surface water sources were large rivers, but several smaller creeks and brooks were also included. Stationary bodies of water from which samples were taken included lakes, ponds, and reservoirs as well as treatment plant intakes.

Sample preparation and preservation. The samples received (usually refrigerated) were either analyzed immediately or stored and preserved according to *USEPA Methods*.[7] Samples for TKN, nitrate, and TOC were preserved, adjusted to a pH of 1.5 with sulfuric acid, and refrigerated for up to 1 week. Samples to be analyzed for iron were preserved with 2 mL HNO_3 (nitric acid) to pH 2. Analysis for sulfides, phosphate, turbidities, and chlorine demand were done immediately, thus avoiding preservation. Samples for sulfate and suspended solids were refrigerated.

As each sample was received, it was filtered and subjected to separate analysis. The original sample was analyzed for the various parameters (designated as raw water). To separate the turbidity particles from the rest of the sample, a portion of each sample was filtered through a 0.45-μm membrane filter. The liquid passing through the filter was analyzed separately (designated as the filtrate). The substance deposited on the filter was washed off and reconstituted up to 1 L with demand-free reference water* for separate analyses (designated as the residue). If the residue was too small to recover, the residue analysis value was calculated as the difference between the raw water and the filtrate analysis results.

Analysis procedures for chlorine demand. All samples were subjected to a 30-min chlorine demand analysis at room temperature. An amount of free chlorine solution, calculated as two times the amount of suspected chlorine demand, was added to the samples. The samples were then mixed and the residual chlorine was measured after 30 min. (The original amount of added chlorine minus the residual equals the chlorine demand.) If all or more than 85 percent of the chlorine was consumed by the sample, a larger amount was added to another portion of the sample to establish a definite residual. Typically, 3 to 5 mg Cl/L was added to samples that were visually classified as "dirty" and 1 mg Cl/L to samples visually classified as "clean."

TABLE 1
Relationship of turbidity to chlorine demand in raw water samples

Number of Samples	Turbidity Range *ntu*	Chlorine Demand—*mg/L* Range	Average in Raw Water	Average in Filtrate	Percent in Filtrate	Average in Solids	Percent in Solids
40	0.05–1	0–1	0.68	0.53	99.1	0.005	0.9
56	>1–5	0.1–7.6	1.21	1.41	96.0	0.062	4.0
21	>5–20	0.72–2.95	1.69	1.82	93.0	0.14	7.0
12	>10–20	0.5–2.9	2.02	1.86	90.0	0.21	10.0
31	>20–170	1.08–4.9	2.69	2.09	77.0	0.60	23.0
All samples	0.05–170	0–7.6			90.0		10.0

TABLE 2
Relationship of turbidity in raw water sources to chlorine demand

Source	Number of Samples	Turbidity Range *ntu*	30-min Cl_2 Demand	TOC *mg/L*	Suspended Solids *mg/L*
Streams	77	0.5–170	0.05–7.8	0.76–8.48	0.3–745.6
Lakes and ponds	33	0.1–28	0*–7.6	0.67–19.6	0.42–51.1
Treatment plant intakes	36	0.005–23	0*–3.25	1.3–8.0	0–33.5
Wells	14	0.3–32	0*–3.7	0.5–4.83	0.1–14.6
All samples	160	0.05–170	0*–7.8	0.5–19.6	0–745.6

*Less than 0.01 mg/L

Total organic carbon and VOC analyses were done according to part 505 of *Standard Methods*, with the use of a commercial analyzer.‡ For solids the TOC was calculated as the difference between the results obtained for raw and filtered samples. Iron and other metal ions were analyzed according to part 303 of *Standard Methods*, using an atomic absorption spectrophotometer.§ Nitrogen was analyzed via nesslerization after standard digestion and distillation methods, according to *Standard Methods*, part 420. Suspended solids and volatiles were done according to *Standard Methods*, part 209. Nitrates were determined using a brucine method, part 213C of the thirteenth edition of *Standard Methods*.[10] Total phosphates were analyzed according to part 424F, and sulfides according to part 427C in *Standard Methods*.

Other contributing factors, including EDTA hardness, were analyzed according to *Standard Methods*, part 31B. Suspended solids (nonfilterable residue) were analyzed according to part 209G, and microbiological counts were performed on the raw water only, using part 909 of *Standard Methods*. Total dissolved solids (TDS) were estimated with a conductivity meter.** A particle counter,†† using 250-, 100-, 70-, and 15-μm apertures and a 4-percent NaCl-H_2O isotone with no dispersant, was used for particle size analyses. A turbidimeter‡‡ was used to measure turbidity. In all analytical procedures, standard laboratory quality assurance controls were used. Known amounts of chlorine standards and USEPA check samples were used to verify analytical methods.

Turbidity stability study. In this study, water supply samples were measured for turbidity over a seven-day period. Turbidity was measured on receipt of the sample (day zero) and, in an attempt to duplicate the original conditions, the samples were shaken. Eighty-nine samples were also measured for turbidity at one, three, and seven days. In an effort to duplicate the original particulate conditions during collection, the samples were shaken before each turbidity measurement. Concomitant with turbidity measurements, the samples were analyzed for TDS, TOC, EDTA hardness, and suspended solids. Particle size distributions were determined for several samples. These parameters were analyzed to ascertain any possible relationships between these factors and turbidity storage stability.

Results and discussion

Demand–turbidity relationship. The distribution of chlorine demand between

*Milli-Q reagent-grade water system, Millipore Corp., Bedford, Mass. *NOTE:* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
†Amperometer A-790, Wallace and Tiernan, Belleville, N.J.
‡DC54, Dohrmann Envirotech, Santa Clara, Calif.
§Model 2001A, Hach Co., Loveland, Colo.
**Model S32T1, Myron L. Co., Encinitas, Calif.
††Model TA11, Coulter Electronics Inc., Hialeah, Fla.
‡‡Model 2001A, Hach Co., Loveland, Colo.

TABLE 3
Summary of correlation coefficients

	Chlorine Demand		Total Coliforms	Volatiles in Residue	Suspended Solids	VOC Residue
	Raw Water	Residue				
Chlorine demand			0.38		0.36	
Cl_2 demand residue				0.54		
Turbidity	0.39	0.47	0.70	0.86	0.91	0.5
Turbidity—*0-10ntu*		0.32	0.34			
Turbidity—*10-20 ntu*	0.36	0.35	0.63			
Turbidity—*>20 ntu*	0.30	0.51	0.68			
Turbidity—*>30 ntu*	0.22					
Turbidity—*>50 ntu*	0.02					
TOC	0.73			0.38		
TOC residue		0.47		0.47	0.47	0.21
TOC—*0-10 ntu*	0.75					
TOC—10-20 ntu	0.90					
TOC—*>20 ntu*	0.61					
TOC filtrate	0.74					
Large particles—*>1 μm*		0.31	0.43	0.31		
Medium particles—*0.5-1 μm*		0.24	0.19	0.24		
Small particles—*<0.5 μm*		0.51	0.29	0.51		
Volatiles in residue		0.54				0.38
Total dissolved solids	0.36					
Iron	0.38					
Ammonia	0.13					
TKN	0.40					
TKN residue						0.29

TABLE 4
Turbidity changes in raw water samples after storage for one day at room temperature

Initial Turbidity *ntu*	Number of Samples	Turbidity Changes After Storage					
		Increase		Decrease		No Change	
		Number	Percent	Number	Percent	Number	Percent
0.05-1	22	8	36	5	23	9	41
>1-5	39	21	54	6	15	12	31
>5	28	10	36	11	39	7	25
Total	89	39	44	22	25	28	32

TABLE 5
Turbidity changes in raw water samples after storage for seven days at room temperature

Initial Turbidity *ntu*	Number of Samples	Turbidity Changes After Storage					
		Increase		Decrease		No Change	
		Number	Percent	Number	Percent	Number	Percent
0.05-1	22	8	36	9	41	5	23
>1-5	39	21	54	14	36	4	10
>5	28	13	46	14	50	1	4
Total	89	42	47	37	42	10	11

TABLE 6
Percent turbidity changes in raw water after storage

Turbidity Change *percent*	One-Day's Storage				Seven-Days' Storage			
	Number with Decreased Turbidity	Percent of Total	Number with Increased Turbidity	Percent of Total	Number with Decreased Turbidity	Percent of Total	Number with Increased Turbidity	Percent of Total
1-10	11	12	13	15	8	9	7	8
10-20	10	11	11	12	13	15	11	12
20-50	1	1	13	15	12	14	14	16
>50	0	0	2	2	4	4	10	11
Subtotal	22	25	39	44	37	42	42	47
No change	28	31			10	11		
Total	89	100			89	100		

the filtrate and solids portions of raw water samples passed through a 0.45-μm membrane filter is shown in Table 1. Approximately 90 percent of the chlorine demand in raw water samples is attributed to the filtrate portion of the samples, and only 10 percent to the solids portion. Sample data are presented in turbidity ranges with corresponding average demands. As the ranges increase, the percent demand attributed to the solids increases. Over the entire range, however, the chlorine demand of the dissolved substances (filtrate) is much greater than that attributed to the solids. Also, in general, as turbidity increases, chlorine demand also increases. A plot of demand and turbidity data is given in Figure 1.

Sources and chlorine demand characteristics of the 160 raw water samples are shown in Table 2. Stream samples, the largest group, showed the greatest range for turbidity and chlorine demand. Lake and pond samples, although ranging to nearly the same chlorine demand levels as stream samples, were substantially lower in turbidity. Chlorine demand of samples from treatment plant intakes and well samples were substantially lower than those of streams and lakes, although turbidity maximums were similar to those of the lake samples. Of 40 samples in the 0.05- to 1-ntu turbidity range, 8 had chlorine demands below the limit of detectability. Total organic carbon values were greatest in the lake and pond samples. Stream samples showed the widest range in suspended solids.

To account for what could be a primary factor in chlorine demand, in addition to turbidity and Cl_2, each water sample was analyzed for TOC, TKN, suspended solids, volatiles in suspended solids, and inorganics. Linear correlation coefficients between parameters are presented in Table 3.

From the summary in Table 3, several generalizations can be made. Although turbidity is defined as an optical property, a strong relationship (0.914) exists between turbidity and suspended solids. Volatile content in residues has a strong correlation to turbidity and a positive correlation to TOC in the residues. Total organic carbon has a strong correlation with chlorine demand, particularly when turbidity was less than 20 ntu in the filtrate. A strong correlation is also seen between turbidity and coliforms, indicating that where particulate matter is present, coliforms can exist. Although the relationship between chlorine demand versus turbidity is positive, it is less than 0.5, and the correlation coefficient decreases at lower turbidity ranges. Considering the particle size in solids versus residue Cl_2 demand, the smaller (0–0.5 μm) particles show a closer relationship to demand than do the larger (0.5–1.0 μm) particles. A strong correlation, however, does not exist.

Turbidity stability. Several generalizations can be made regarding turbidity changes over a seven-day period. Turbidity changes are greater over seven-day than over one-day periods of storage (Tables 4 and 5). Turbidity changes in the shaken samples over time are evident. Forty-four percent showed an increase in turbidity and 25 percent a decrease for 1-day storage. Over seven days, 47 percent showed an increase in turbidity and 42 percent a decrease. The magnitude of turbidity changes in stored samples are reflected in Table 6, ranging from a 200-percent increase to a 40-percent decrease. Although the nature of turbidity is important, it is not easily identified or quantified. Because there is no convenient way to measure particulates (especially those that may protect pathogens), turbidity is used as a surrogate parameter. Utilities are encouraged to supply low turbidity waters because the turbidity particles may protect pathogens, shielding them from the disinfection agent.[4] This, of course, provides uncertainties because inorganic particles probably pose no danger, whereas even small organic particles may protect the pathogens.

McGirr examined the storage stability of turbid water samples and concluded that when samples are stored for periods of five to seven days, turbidity drops 20–30 percent.[11] The cause of this drop was attributed to agglomeration of suspended particles rather than to a "plating out" of the hard crust of suspended matter. Because the study participants used different instruments to measure turbidity and various methods to shake samples before analysis, high precision and accuracy was difficult to obtain. The author also saw no direct relationships among residues, mass of solids, and turbidities.

From this study's statistical data, 89 percent of the samples manifested instabilities or changes in turbidity over the seven-day period (Table 4). These instabilities were also reflected during one- and three-day holding times. In contrast to the McGirr study, this study showed that when samples were stored, about half the turbidity measurements increased and about half decreased. This may result from a breaking down of larger particles (the opposite of agglomeration). Apparently the forces controlling turbidity are complex, interacting, and variable.

Conclusion

The correlation between chlorine demand and turbidity is not strong and turbidity cannot be used as an accurate indicator for chlorine demand. Because 90 percent of the demand remains in the filtrate, it is the chemical nature of the water that exerts the disinfection demand. As expected, TOC has a strong relationship to demand and occurs largely in the filtrate. If any demand is exerted by the particulate matter, it is the nature, not the size, of the particles that is responsible for demand. Because the data indicate changes in turbidity occur during storage of samples, analyses should be done at the time and site of collection to ensure accuracy of turbidity readings.

References

1. HACH, C.C. Understanding Turbidity Measurement. *Indus. Water Engrg.*, 9:18 (1972).
2. HOFF, J.C. The Relationship of Turbidity to Disinfection of Potable Water. *Evaluation of the Microbiology Standards for Drinking Water* (C.W. Hendricks, editor). USEPA 570/9-78-00C, Washington, D.C. (1978).
3. STOVER, E.L. & MARKS, P.J. Development of Suspended Solids Quality Control and Performance Evaluation Samples. USEPA-600/4-76-052, Cincinnati, Ohio (Oct. 1977).
4. SYMONS, J.M. & HOFF, J.C. Rationale for Turbidity Maximum Contaminant Level. 1975 AWWA WQTC, Atlanta, Ga.
5. MESCAN, A.R. Turbidity Quality Control, Contract 68-03-2490. USEPA, Environ. Monitoring and Support Lab., Cincinnati, Ohio (1977).
6. *Standard Methods for the Examination of Water and Wastewater.* APHA, AWWA, and WPCF, Washington, D.C. (15th ed., 1981).
7. Methods for Chemical Analysis of Water and Wastes. USEPA-600/4-79-020. Cincinnati, Ohio (March 1979).
8. *Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water.* USEPA-600/8-78-008, Cincinnati, Ohio (March 1978).
9. THOMAS, R. ET AL. Community Water Supply Survey, Technical Support Div., USEPA (unpublished).
10. *Standard Methods for the Examination of Water and Wastewater.* APHA, AWWA, and WPCF, Washington, D.C. (13th ed., 1971).
11. MCGIRR, D.J. Turbidity and Filterable and Nonfilterable Residue. Interlaboratory Quality Control Study 10, Rept. Series 37. Inland Waters Directorate, Canada Center for Inland Waters, Burlington, Ont. (1974).

About the author: *Edward L. Katz, a research chemist formerly with the Microbiological Treatment Branch (MTB), is now with the Thermal Destruction Branch, Hazardous Waste Engineering Research Laboratory, USEPA, 26 W. St. Clair St., Cincinnati, OH 45268. Katz worked on disinfection studies for the past 10 years while with the MTB. He is a graduate of the Georgia Insitute of Technology.*

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.